HIGH PRESSURE CO_2 SEPARATION USING MEMBRANES: MEMBRANE SELECTION AND PROCESS MODELING

by

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Sincerely,
Jimoh K. ADEWOLE
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LIST OF SYMBOLS

A_m	membrane area (m^2)
C	gas concentration
C_1	cost of membrane element
C_2	cost of permeator module
C_3	cost of labour
C_4	cost of hydrocarbon loss
C_h	gas concentration at the upstream
CH_{4f}	concentration of CH_4 in the feed streams
CH_{4s}	concentration of CH_4 in the sweet streams
C_l	gas concentration at the downstream
C_{mob}	gas concentration with finite mobility
D	diffusion coefficient
D_0	diffusion coefficient at zero concentration in the polymer matrix
D_D	diffusion coefficient in the Henry site (cm^2/s)
D_H	diffusion coefficient in the Langmuir site (cm^2/s)
E_D	activation energies of diffusion
E_{di}	dispersive cohesive energy
F	fraction of Langmuir sorption species having a finite mobility
F_{di}	dispersive molar attractive constant

F_{pi}	polar molar attractive constant
H_S	heats of solution
p	pressure (bar)
P_A	permeability of fast gas (CO_2) (kmol.m/m^2.s.bar)
p_h	feed/upstream gas pressure (bar)
p_l	downstream/permeate gas pressure (bar)
p_{pl}	plasticization pressure (bar)
Q	quantity of gas
q_f	feed flow rate in kmol/s
q_p	permeate flow rate in kmol/s
q_r	retentate flow rate in kmol/s
ℓ	membrane thickness (m)
t	time (sec)
T_g	Glass Transition Temperature
t_m	Membrane life (years)
V	molar volume
X_i	numerical value of the property
$X_{\max}$	maximum value in the list of the property
$X_{\min}$	minimum value in the list of the property.
x_o	concentration of CO_2 in the retentate (product) (mol%)

Y_i	scaled membrane properties
y_p	concentration of CO_2 in the permeate (mol%)

Greek Symbols

θ	stage - cut
β	empirical parameter representing the extent of the concentration dependence of the diffusion
ϕ	constant value or varies with feed pressure
α_i	Weighting (scaling) factor
α	selectivity
$\alpha_{A/B}$	selectivity of *A* in preference to *B*
γ	performance index
$	US Dollar
δ_d^2	dispersive solubility parameter
δ_p^2	polar solubility parameter
δ_h^2	hydrogen solubility parameter
δ_t	total solubility parameter

LIST OF ABBREVIATIONS

6FDA	2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride
ANN	Artificial Neural Network ,
APTMDS	bis (3-aminopropyl)-tetramethyldisiloxane)
BAS	Bis (aminopropyl) polydimethylsiloxane
BCM	Billion Cubic Meters
CD	Cyclodextrin
CH_4	Methane
CMS	Carbon Molecular Sieve
CO_2	Carbon dioxide
cpm	cost per unit mass (US$/kg)
CRC	Capital Recovery Cost ($)
HLC	Cost of Hydrocarbon Loss (US$/MMBTU)
DADE	Diamino diphenyl ether
DCM	Dichromethane
DDBT	3,7-diaminodibenzothiophene-5,5′-dioxide
DEG	Diethylene Glycol Dimethyether

DMAc	N,N-Dimethylacetamide
DMF	N,N-Dimethylformamide
DMSO	Dimethyl Sulfoxide
dop	Density of polymer (kg/m^3)
EC	Cost of Energy ($kW^{-1}hr^{-1}$)
EtOH	Ethanol (EtOH)
EVA	ethylene vinyl acetate
FFV	Fractional Free Volume
GLY	Glycerol (GLY)
GPU	Gas Permeation Unit
HAB	3,3'-dihydroxy-4,4'-diamino-biphenyl
IPCC	Intergovernmental Panel on Climate Change
LC	Cost of Labour (US$/hr)
LMWC	Low Molecular Weight Compounds
MC	Maintenance Cost (US$)
OE	Operating Expenses (US$)
MEC	Cost of Membrane Element (US$/$m^2$)

MeOH	Methanol
MGS	Membrane gas separation
MMC	Membrane module manufacturing cost (US$/$m^2$)
MMSCFD	Million Standard Cubic Feet
MRC	Membrane Replacement Cost (US$/$m^2$)
NG	Natural gas
nm	nanometer
NMP	1-Methyl-2-pyrrolidone
PALS	Positron Annihilation Lifetime Spectroscopy
PBI	Poly (benzimidazole)
PBO	Polybenzoxazoles
PBT	Polybenzothiazoles (PBT)
PDMC	propane – diol monoesterified cross – linkable polyimide
PDMS	Poly (dimethyl siloxane)
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PHA	Polyhydroxyamide

PI	Polyimide
PPO	Poly (2, 6-dimethyl-1,4-phenylene oxide)
PSF	Polysulfone
PTFE	Polytetrafluoroethylene
PTMS	Poly[1-(trimethylsilyl)-1-propyne]
S-PEEK	Poly (ether ether ketone)
STP	Standard Temperature and Pressure
SVM	Support Vector Machine
SVR	Support Vector Regression
TCDA	2,3,5-tricarboxy cyclopentyl acetic dianhydride
TCI	Total Capital Investment
TGA	Thermo Gravimetric Analysis
THF	Tetrahydrofuran
TOC	Total Operating Cost (US$)
TW	Tera watt
XRD	X-ray diffraction

PEMISAHAN CO_2 PADA BERTEKANAN TINGGI MENGGUNAKAN MEMBRAN: PEMILIHAN MEMBRAN DAN PEMODELAN PROSES

ABSTRAK

Pemisahan CO_2 daripada gas asli (NG) telah menarik minat penyelidikan kerana permintaan tenaga yang semakin meningkat dan keperluan teknik penulenan gas yang lebih cekap dan mesra alam. Kebanyakan NG dihasilkan bersama CO_2 yang perlu disingkirkan demi untuk meningkatkan nilai kalorinya. Teknologi membran merupakan salah satu teknologi yang digunakan secara meluas untuk penyingkiran CO_2. Walau bagaimanapun, pasarannya masih kecil berbanding proses-proses pemisahan gas yang lain. Ini adalah kerana penggunaan bahan-bahan membran dengan prestasi pemisahan yang rendah dan keadaan pengoperasian modul yang tidak optimum. Pengoptimuman bersistematik bagi setiap peringkat penyediaan membran dan operasi modul bertekanan tinggi telah dicadangkan untuk menyelesaikan masalah tersebut.Salah satu cabaran utama operasi bertekanan tinggi adalah fenomena kesan penusukan pemplastikan yang disebabkan oleh peningkatan tekanan suapan.

Polimer komersil polisulfona telah diubahsuai untuk mengoptimumkan prestasi pemisahannya. Kajian bertekanan tinggi dan pemodelan matematik telah dijalankan untuk menilai prestasi pemisahan membran. Bagi mewujudkan tekanan suapan yang tertinggi semasa penyingkiran CO_2 tanpa pemplastikan, ciri-ciri pemisahan membran telah dikaji menggunakan ujian penelapan pada tekanan mencecah 57 bar. Kajian dinamik bagi prestasi membran juga dilakukan menggunakan ujikaji penelapan bagi tempoh masa antara 5 hingga 1080 jam (45 hari) dengan pelbagai tekanan antara 6 hingga 57 bar. Model matematik telah

dibangunkan berdasarkan teori “dual-sorption” dan model keseluruhan tidak bergerak. Proses pengoptimuman untuk pemilihan membran telah dicapai dengan menggunakan kaedah pengoptimuman pelbagai objektif, manakala keadaan operasi modul dicapai menggunakan model pengaturcaraan pengoptimuman kekangan non-linear dan algoritma “Golden search” yang dilaksanakan menggunakan MATLAB.

Tekanan pemplastikan bagi membran yang disediakan adalah 41.07 bar manakala kebolehtelapan dan kememilihan pada tekanan ini adalah masing-masing 5.99 Barrer, dan 44.19. Ini merupakan peningkatan sebanyak 17.65% bagi tekanan pemplastikan dan 66.39% bagi kebolehtelapan. Walau bagaimanapun, membran tersebut kehilangan kira-kira 79.65% kebolehtelapannya pada tekanan ini manakala kememilihannya meningkat sebanyak 91.13% jika dibanding dengan nilai pada 5 bar. Ujian kebolehtelapan yang bergantung kepada masa mendedahkan bahawa tekanan pemplastikan sebagai titik keseimbangan boleh digunakan sebagai kekangan dalam pengoptimuman proses pemisahan gas membran. Model matematik yang dibangunkan menunjukkan keupayaan ramalan yang sangat baik untuk tekanan pemplastikan. Pemilihan bahan membran juga didapati mampu dioptimumkan dengan cekap dengan menggunakan kaedah pengoptimuman multi-objektif.